

Abstract No. DiMa0149

**Growth Rate of Polymer-Induced Calcium Carbonate Films: Concentration and CO<sub>2</sub> Dependence**

E. DiMasi (BNL), V.M. Patel, M.J. Olszta, M. Sivakumar, G. Sivakumar, Y.P. Yang, and L.B. Gower (U. Florida)  
Beamline(s): X22B

**Introduction:** In biogenic and biomimetic mineral nucleation, macromolecules are present which can dictate the manner in which the mineral forms, including control of the crystal size, morphology, polymorph, and even the stabilization of amorphous phases of minerals which in the absence of the macromolecules would be crystalline. Molecules known to affect crystallization in solution include the proteins in living systems as well as acidic synthetic polymers. It is strongly believed that the insoluble organic “scaffolds” present in many biomaterials may direct mineral nucleation as well. However, the details of such mechanisms are unclear and in most cases have not been verified by atomic-scale in-situ structural measurements.

**Methods and Materials:** We have studied calcium carbonate films nucleated at liquid surfaces. Escape of CO<sub>2</sub> gas increases the CaCO<sub>3</sub> supersaturation and drives mineralization. A fatty acid (CH<sub>3</sub>[CH<sub>2</sub>]<sub>18</sub>COOH) monolayer provides a template, and dilute polyacrylic acid (PAA) in solution forces mineralization to proceed through an amorphous precursor phase that forms a solid film at the template interface [1]. Films were grown in Langmuir troughs with area ~300 cm<sup>2</sup> and depth of either 2 or 6 mm, and contained in a helium environment at T=19°C. The surface structure was studied by x-ray reflectivity and grazing-incidence diffraction methods during mineralization using the Harvard/BNL Liquid Surface Spectrometer.

**Results:** Reflectivity measurements allow us to extract surface-normal density profiles (Figure 1a), allowing us to determine the thickness and density of the amorphous precursor film as it grows under various conditions. Early profiles, 1.5 hours or less from preparation of the sample, show a peak of density where Ca<sup>2+</sup> ions collect at the fatty acid headgroups. At later times, a dense region appears between the monolayer and the water subphase, showing that an amorphous film has formed. The time dependence of the film thickness for a PAA concentration of 32 µg/ml (Figure 1b) was found to depend drastically on the trough depth — in other words, on the rate of CO<sub>2</sub> gas escape. No evidence was found in diffraction for any atomic-scale templating effects of the monolayer, which instead apparently nucleates the amorphous film by changing the local cation concentration. Since the COO<sup>-</sup> groups of the PAA would also be expected to affect cation concentration, we explored a range of PAA concentrations, studying the effect on film growth and stability in the 2mm deep trough (Figure 1c). At high PAA concentrations, the CO<sub>2</sub> escape is evidently rate limiting. Films grown under these conditions are smooth and stable for 10-30 hours, after which they dissolve without crystallizing. With smaller PAA concentrations, the amorphous film is less stable, enabling crystallization into primarily calcite. All of our results indicate that kinetics, not templating, controls mineralization in calcium carbonate films. Future work will be directed towards a more quantitative understanding of these kinetic factors.

**Acknowledgments:** L.B.G. acknowledges support from NSF CAREER Grant DMR-0094209 and the National Institutes of Health (DK59765-01). E.D. received support from the BNL LDRD program (Project No. 02-67). The National Synchrotron Light Source is supported under USDOE Contract DE-AC02-98CH10886.

**References:**

[1] E. DiMasi, V. M. Patel, M. Sivakumar, M. J. Olszta, Y. P. Yang, and L. B. Gower, Langmuir (in press, 2002).

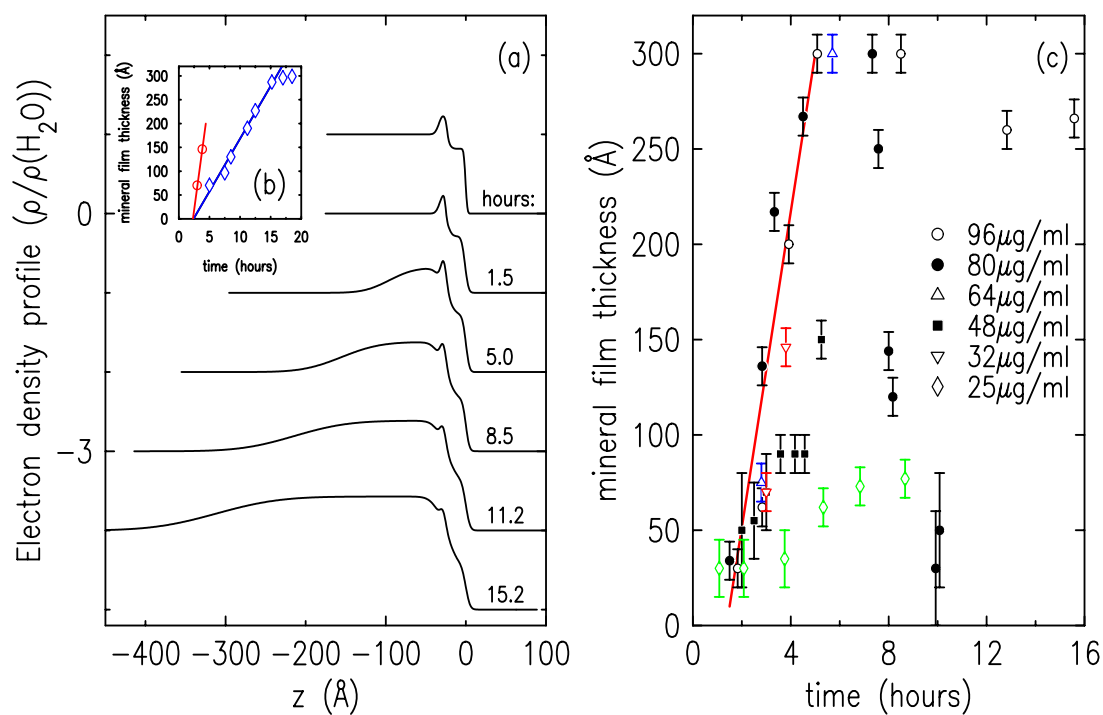


Figure 1. (a) Time series of surface-normal electron density profiles for an arachidic acid monolayer assembled on a supersaturated calcium carbonate subphase with 32  $\mu\text{g/ml}$  poly(acrylic acid, sodium salt) in a 6mm deep trough. Early profiles show regions occupied by hydrocarbon tails, headgroups, and bound cations. Late profiles show an additional dense region, eventually extending hundreds of Å into the subphase, corresponding to an amorphous mineral film. (b) Thickness as a function of time for the sample in (a) (diamonds), and for a similar solution nucleated in the shallower 2mm trough (circles).  $\text{CO}_2$  gas escapes faster from the shallow pan and increases the mineralization rate. (c) Time dependences of film thicknesses for varying PAA concentrations in the 2mm trough.